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Investigation of Vanadium Substituted Heteropoly Acids for n-Butane Selective Oxidation

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Introduction: Selective oxidation of n-butane is used to produce maleic acid and subsequently maleic anhydride (MA). MA is used for polyester resins and as intermediates for other chemicals such as tetrahydrofuran. Current commercial catalysts for conversion of n-butane to MA are based on vanadium pyrophosphate oxide (V-P-O). Use of heteropoly acid (HPA) catalysts such as molybdophosphoric acid ($\text{H}_3\text{PMo}_{12}\text{O}_{40}$) and its derivatives for this reaction has also been investigated. Since HPAs contain both acid and oxidizing properties, it may be possible to produce highly active catalysts from these materials. These catalysts often incorporate V into the structure as a substitute for one of the Mo atoms and as cations exchanged for the protons. One goal of our work is correlate the activity and local environment under reaction conditions for the different types of V precursor.

Methods and Materials: In situ x-ray absorption spectroscopy (XANES and EXAFS) at the V K edge was used to determine the oxidation state and structural parameters of V containing HPAs. Catalyst materials with vanadium incorporated into the structure ($\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ and $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$) and vanadium cation exchanged ($\text{VPMo}_{12}\text{O}_{40}$) catalysts were studied during the selective oxidation of n-butane to maleic acid. The samples were pretreated in flowing helium and then exposed to a reactant feed mixture of 4:2:4:5 ml/min of n-butane:oxygen:helium:water at 380 C. All catalysts had been previously tested for reactivity in the laboratory.

Results: Laboratory reactivity testing showed similar activity results for all three catalysts. For the $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ sample, selectivity to MA was 18% with selectivity to CO_x of 38%. For the $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ sample, MA selectivity was similar; however, selectivity to CO_x increased to 51% at the expense of other minor products. In contrast, for the $\text{VPMo}_{12}\text{O}_{40}$ sample, selectivity to MA was only 3% with ethylene and propylene being the major products.

Preliminary analysis of the x-ray absorption spectroscopy for the three catalyst samples indicates that V is initially in the +5 oxidation state. As the samples are pretreated, the V is partially reduced to approximately a +4 oxidation state. The V also remains partially reduced when exposed to the reactant mixture. EXAFS analysis also indicates that the local structure around the V is similar following pretreatment and during exposure to the reactant mixture. Complete analysis of the XANES and determination of structural parameters from the EXAFS is currently underway.

Conclusions: Although activity results differ depending on the type of V in the as made sample, preliminary results indicate that both oxidation state and local structure around the V under reaction conditions are similar regardless of the type of V precursor.

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